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Development of a thermoeconomic methodology for the optimization of biodiesel production—Part I: Biodiesel plant and thermoeconomic functional diagram

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ABSTRACT

This work developed a methodology that uses the thermoeconomic functional diagram applied for allocating the cost of products produced by a biodiesel plant. The first part of this work discusses some definitions of exergy and thermoeconomy, with a detailed description of the biodiesel plant studied, identification of the system functions through Physical Diagram, calculation of the irreversibilities of the plant, construction of the Thermoeconomic Functional Diagram and determination of the expressions for the plant's exergetic functions. In order to calculate the exergetic increments and the physical exergy of certain flows in each step, the Chemical Engineering Simulation Software "HYSYS 3.2" was used. The equipments that have the highest irreversibilities in the plant were identified after the exergy calculation. It was also found that the lowest irreversibility in the system refers to the process with a molar ratio of 6:1 and a reaction temperature of 60 °C in the transesterification process. In the second part of this work (Part II), it was calculated the thermoeconomic cost of producing biodiesel and related products, including the costs of carbon credits for the CO_2 that is not released into the atmosphere, when a percentage of biodiesel is added to the petroleum diesel used by Brazil's internal diesel fleet (case study).

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1. Introduction

In pursuit of sustainable development, saving energy and developing rational technologies for its generation became a major objective, taking into account the related effects to the

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Nomenclature

φ	Chemical exergy relation
b_i	Chemical exergy [kW]
CO_2	Carbon dioxide
Ex	Total exergy [kW]
ex	Specific exergy [kJ/kg]
h	Specific enthalpy [kJ/kg]
I	Irreversibility [kW]
M	Mass flow [kg/s]
P	Pressure [kPa]
P_0	Reference pressure [kPa]
LHV	Lower heating value (Q_i) [kJ/kg]
s	Specific entropy [kJ/kg/K]
S	Entropy [kJ]
s_0	Specific entropy (reference) [kJ/kg/K]
T	Temperature [°C]
Tm	Thermodynamics
T_0	Room temperature [K]
Y	Exergetic function in incremental base [kW]
$Y_{i,j}$	jth input to the ith unit [kW]
$Y_{i.k}$	kth output to the ith unit [kW]

environment. In addition, the impending shortage of fossil fuels required humanity to rationally use the primary energy and, consequently, new technologically developed versions of power plants have been designed in order to increase not only the energy efficiency but also the exergy and ecological efficiency. In this sense, biodiesel appears as a biodegradable biofuel and environmentally friendly, with properties similar to the conventional diesel, but with low greenhouse gases emission profile.

The purpose of this paper (Part I) is to development a thermoeconomic analysis of biodiesel production, considering the irreversibilities in each stage of a biodiesel production plant, enabling the achievement of biodiesel production costs and the main byproduct generated: glycerin. Basically, an algebraic method based on the combination of the cost analysis was developed, suggested by Silveira [1], with the exergy analysis incorporating the costs of carbon credits for the CO_2 that is not released into the atmosphere, when using a percentage of biodiesel in regular diesel used by the internal fleet of diesel vehicles in Brazil (Part II).

1.1. Exergy

According to Kotas [2] and Szargut [3], the exergy can be divided into four parts: kinetic, potential, thermo-mechanical and chemical. The thermodynamics or physical exergy is defined as the maximum work obtained in reversible processes when a quantity of material is taken from the initial state (P and T) to obtain the equilibrium state in a pressure and temperature reference (T_0 and P_0) [3].

For real processes, the exergy input on a component of the plant is always greater than the exergy output, when there is no external force (work) applied on it. This lack of balance is due to the irreversibilities present in the process. According to Wall [4], the conceptual distinction between these two losses is due to the irreversibilities. Using the Eq. (1) and knowing the specific properties such as enthalpy, entropy and temperature of reference, it is possible to calculate the thermo mechanical exergy.

$$ex^{Tm} = (h - h_0) - T_0(s - s_0) \tag{1}$$

In the case of liquid and solid fuels, the determination of exergy is not so simple, because these fuels are solutions of numerous chemical compounds, usually of unknown nature. According Szargut [3] and Kotas [2], the ratio of chemical exergy to lower heating value (LHV) for gas and liquid fuels, is the same as for pure chemicals. This relationship (Eq. (2)), called by the Greek letter φ, is as follows:

$$\varphi = \frac{b^0}{(PCI)^0} \tag{2}$$

where b^0 is the chemical exergy and LHV is the lower heat value [kJ/kg]. For liquid fuels, the ratio φ is dimensionless and is expressed in the following experimental formula:

$$\varphi = 1.0401 + 0.1728 \times \frac{h}{c} + 0.0432 \times \frac{o}{c} + 0.2169 \times \left(1 - 2.0628 \times \frac{h}{c}\right) \tag{3}$$

where c and h are the mass fractions of C, H and O, respectively; in this expression, the effect of sulfur is already included in the correlation.

1.2. Irreversible processes

The processes found in nature have some degree of irreversibility. Only the ideal plane processes do not generate friction and there is no heat transfer. All irreversible processes can be identified by three basic features: (i) during the operation there is always dissipation of energy, (ii) occur spontaneously and in one direction, (iii) to occur in the reverse direction, introduction of energy is necessary. The irreversibility (I), which represents the degraded portion of useful work available, is calculated by Eq. (4).

$$I = \sum Ex_{i \times Entrada} - \sum Ex_{i \times Saida} \tag{4}$$

1.3. Thermoeconomic analysis

Currently, there are two main methodologies: the method of cost accounting (exergy cost theory), which uses the average costs as a basis for rational evaluation of costs, and the optimization method (thermoeconomic functional analysis), which uses the marginal costs to minimize product costs of a system or components. The most complete thermoeconomic optimization was the "Thermoeconomic Functional Analysis" which, according to Valero et al. [5], was developed by various researchers such as Evans [6], Frangopoulos [7], Von Spakovsky [8] using as basis the work presented by Evans and Tribus [9]. This method attempts to optimize the design of a plant that does not exist, minimizing an objective function [10].

According to Valero's matrix method [5], Silveira showed a thermoeconomic analysis in a linear programming level, as a selection criterion for cogeneration systems with the use of steam and gas turbines, demonstrating the feasibility of the employment of natural gas in the surveyed systems [11]. In 1998, Silveira developed a new methodology for thermoeconomic optimization of energy systems by addressing the economic aspects associated with the exergy concept to aid in decisions such as equipment selection and mode of operation choice, optimizing the design of thermal plants. In this work, using Frangopoulos' functional diagram of thermoeconomic concept, Silveira determined the specific production costs of heat, cold and power, and used them in the equation of Exergetic Cost of Manufacturing, presented also in this work, as being the production costs of inputs related to

thermal and electrical power (purchased from the greed or produced by the CHP) [1,12,13].

2. Description of the biodiesel plant

The biodiesel production plant studied in this work is a process which was simulated computationally by Zhang in HYSYS Plant NetVers 2.1.3 software developed by Hyprotech Ltd [14,15]. To develop the proposed thermoeconomic methodology in this paper; of the four cases studied by Zhang, only the first process (Production of biodiesel using virgin vegetable oil, methanol and alkali catalysts) was adapted and simulated computationally using the same software. The following presents a brief description of the process as well as data used for computer simulation.

2.1. Process simulation in HYSYS

The procedure for the simulation process involves defining in HYSYS the main chemical components used in biodiesel production, the selection of a thermodynamic model, the choice of plant capacity, choosing the appropriate operating units, as well as the definition of thermodynamic properties (flow, temperature, pressure and other conditions). The software's virtual library provides the necessary information to determine the main chemical components of the process: methanol, glycerol, sodium hydroxide and rapeseed oil were used as the raw material necessary for biodiesel production. Considering the mass fractions of the rapeseed oil, oleic acid has the highest percentage of fatty acids that are part of this oil, so "triolein" $C_{57}H_{104}O_6$ was chosen to represent the rapeseed oil in the HYSYS program. For the thermoeconomic study, the mass fraction of the major fatty acids that make up the rapeseed oil in the HYSYS program was used, but, when mixed to other chemical components, specifically in the output of the transesterification reactor, "triolein" was used to simulate the process.

To simulate the flow of biodiesel, "methyl oleate" $C_{19}H_{36}O_2$ was used as the representing substance of Biodiesel in HYSYS. This chemical formulation is very similar to those used by other researchers in the field in order to determine the chemical composition of biodiesel [16].

Finally, it was selected in HYSYS the thermodynamic model NRTL ("non-random two liquids") to predict the coefficients and components in the liquid phase. The same model in HYSYS was used to help make the thermoeconomic analysis. The same thermodynamic model was also used by Zhang to simulate the four processes.

Rapeseed oil (triolein) is the best alternative, since it does not directly compete with soybeans, the main agricultural crop in Brazil. The grains of rapeseed produced in Brazil are 38% of oil, according to the "Embrapa/Trigo—Passo Fundo (Brazil)", while the soybeans are 18%. Another favorable point is that rapeseed is the third largest commodity in the world, accounting for 16% of the production of vegetable oils.

2.2. Process description

Table 1 shows the main properties and mass flows of the inputs and outputs of each stage of the biodiesel's plant. Fig. 1 shows a diagram of the process in general, which is an adaptation of the first case studied by Zhang and also simulated computationally in Hysys. The main steps are described below:

Transesterification: The transesterification reaction occurs with a 6:1 M ratio (methanol:oil), 1% of sodium hydroxide solution (with respect to oil), a reaction temperature of 60° and 400 kPa. The flow of methanol is 117.2 kg/h (the recycled methanol is 111 kg/h) and the flow of anhydrous sodium hydroxide is 10 kg/h. These flows are pumped and introduced into the transesterification reactor. The crude oil is heated before entering the reactor and the outflow from the reactor goes to the distillation equipment. Methanol recovery: At the output of the vacuum distillation equipment, about 94% of methanol is recovered from the biodiesel coming from the transesterification reactor. Vacuum distillation is used to keep the temperature below 150 °C. The methanol extracted in this process is mixed with fresh methanol flow earlier than in the transesterification process and the outflow of the distiller is sent to a wash column (before the flow is cooled in a heat exchanger in order to reduce the temperature to 60 °C). See Fig. 1. Wash: The aim of this step is to separate the residual methanol, catalyst and glycerol from biodiesel. In this process, 11 kg/h of water at 25 °C is also added. The glycerol (128 kg/h) produced by the process contains: 81% of glycerol, 8% of water, 3% of methanol and 9% of sodium hydroxide. See Fig. 1. Biodiesel Purification: The reactor for biodiesel purification works in vacuum to keep the temperatures low enough to prevent the degradation of biodiesel, and a condenser is used to separate the biodiesel from the methanol and the water. Biodiesel with a purity of 99.65% is obtained as distillate at 194 °C and 10 kPa. The oil that is not converted to biodiesel could also be reintroduced into the reactor for transesterification. Purification of glycerin: After the neutralization step and the removal of the sodium hydroxide, the stream contains 85% of glycerol. The stream goes through a vacuum distillation step to remove the residual water and methanol, obtaining a 92% of pure glycerin. See Fig. 1 to visualize the process in detail.

Data of enthalpy and entropy for each point in the process is obtained from HYSYS and is different from those found in traditional thermodynamic tables for water, air or other chemical compound. This work takes into account the variation of enthalpy and entropy, $(h-h_0)$ and $(s-s_0)$, to calculate the exergy so the

Table 1
Main flow properties at each step of the process [adapted from Zhang et al. [14,15]].

Flow	4	8	5	3	9	10	12	14	16	20	22	17	19	18	23	24
Temp. (°C)	25	26.7	25	60	60	28.2	122.34	70	60	50	60	193.7	193.7	414.7	56.2	112
Pres. (kPa)	100	400	100	400	400	20	30	150	110	110	110	10	10	20	40	50
Flow mass (kg/h)	117.2	238.39	10	1050	1288.4	111.19	1177.2	1177.2	1060.21	128	122.31	7.82	999.88	52.50	9.02	113.29
Mass fraction																
Methanol	1.0	0.956	0.0	0.0	0.092	1.0	0.006	0.006	0.003	0.03	0.032	0.388	0.0	0.0	0.363	0.0
Oil	0.0	0.0	0.0	1.0	0.041	0.0	0.045	0.45	0.050	0.0	0.0	0.0	0.0	1	0.0	0.0
Biodiesel	0.0	0.0	0.0	0.0	0.779	0.0	0.853	0.853	0.946	0.0	0.002	0.504	0.997	0.0	0.0	0.0
Glycerol	0.0	0.0	0.0	0.0	0.081	0.0	0.088	0.088	0.0	0.81	0.85	0.0	0.0	0.0	0.0	0.85
NaOH	0.0	0.044	1.0	0.0	0.008	0.0	0.008	0.008	0.0	0.09	0.0	0.0	0.0	0.0	0.0	0.0
H_2O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.001	0.08	0.117	0.107	0.003	0.002	0.637	0.15
H_3PO_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Na_3PO_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

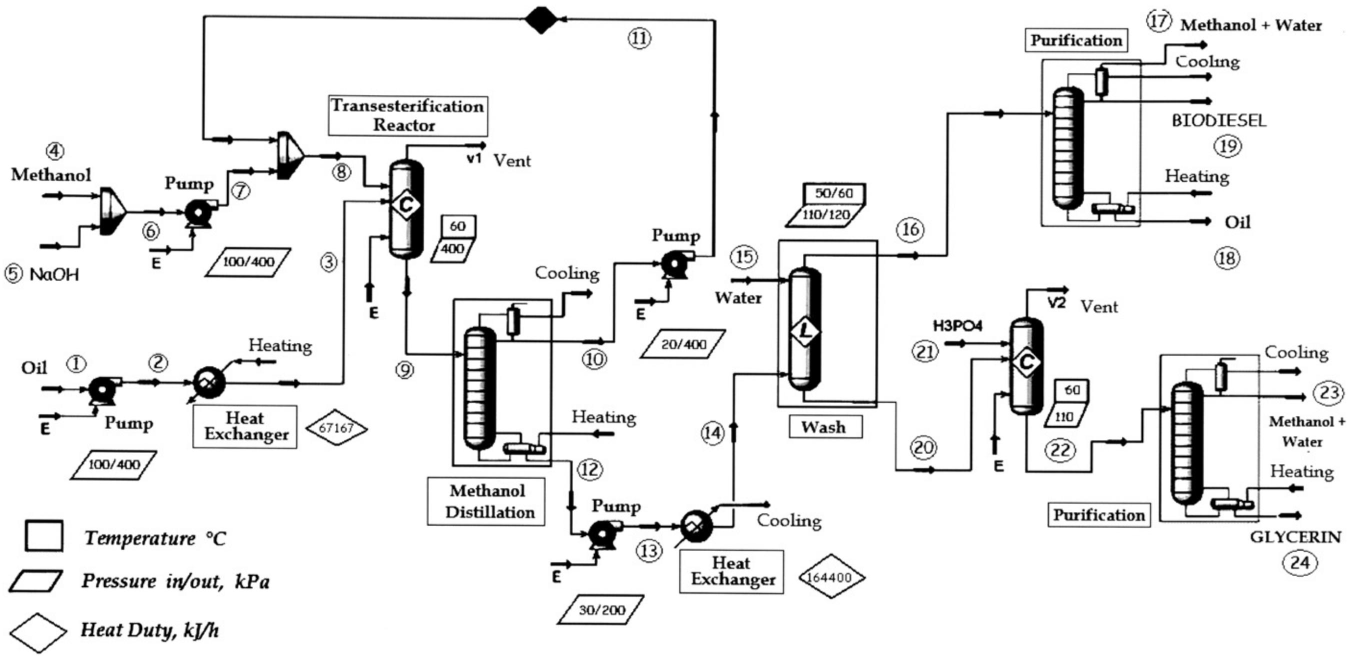


Fig. 1. Biodiesel production process from rapeseed oil diagram.

final result using the data from the HYSYS program is the same as when the thermodynamic tables are used.

3. Methodology

3.1. Identification of system functions

In order to identify the various exergetic functions of the system, a physical representation of the biodiesel plant configuration shown in Fig. 1 was built. Fig. 2 establishes a function of the system as a whole and of each unit individually. The plant under study will produce 8000 t/year of biodiesel with 8000 h of operation, the alcoholic reagent used is methanol and the catalyst base used is NaOH. Finally, the reaction temperature and pressure are 60 °C and 400 kPa, respectively. To calculate the exergy of solid substances used in the process, the specific chemical exergy of the tables presented by Szargut [3] was used. Table 2 presents the results of chemical exergy for liquid substances (Eqs. (2) and (3)) and solids used in BPP (Biodiesel Production Plant).

According to what was previously mentioned, the properties of enthalpy and entropy for each individual point in the diagram are those of reference that were taken from the HYSYS program. These properties vary and depend on temperature, pressure, flow and mass fraction of each point. From the physical diagram in Fig. 2, Table 3 was prepared, which presents all the thermodynamic characteristics of flows in each unit of the plant, these properties are: temperature, pressure, flow, chemical exergy (Eqs. (2) and (3)) and total exergy. (Eq. (1)).

3.2. Calculating the irreversibility for the BPP

The irreversibilities are calculated by Eq. (4) and Table 4 presents all the irreversibilities of equipments from the BPP. This table shows that the highest level of irreversibility of the plant occurs in the transesterification tank, this being the main equipment in a plant that consumes lots of electricity and thermal energy. The cleansers, both for biodiesel and glycerin, which are cleaning and purification equipment, have a moderate consumption of electricity and high consumption of thermal energy, making it the second highest level of irreversibility. Finally, third, are the heat exchangers. Table 5 shows the irreversibility for different reaction temperatures for each molar ratio of the transesterification process. Through the calculation of the irreversibilities of the plant under study, it is evident that the lower irreversibilities in the process are for a molar ratio of 6:1 and a reaction temperature of 60 °C.

3.3. Construction of the thermoeconomic functional diagram

According to the physical diagram shown in Fig. 2, the TFD the plant to produce biodiesel was prepared. This TFD, shown in Fig. 3, is composed of geometric figures that represent the constituent units of the plant, and processes that interact with this plant, as well as a network of lines representing the functions in terms of exergy unit increments, according to the method developed by Silveira [1]. The notation adopted in this functional diagram is the same as the one suggested by Frangopoulos [7].

3.4. Determination of the expressions for the exergetic functions

To determine the exergetic functions associated with the TFD, losses in the pipes will not be taken into account. Considering the physical diagram and the values of thermodynamic properties for each flow of the process steps, the values of exergy flows in the associated incremental basis functional thermoeconomic diagram, shown in Fig. 3, are determined. Table 3 presents the calculation of physical exergy that, when added to the chemical exergy, gives the total and specific exergy associated to the streams. The equations shown below are used to calculate the exergy increment in each step of the process, according to the functional thermoeconomic diagram. Finally, Table 6 presents the values of exergetic functions associated to the units described in both physical and functional thermoeconomic diagram, obtained by the equations below.

UNIT 1: Pump (B1)

$$Y_{1.1} = Y_{0.3} = m_1 \times ex_1 \quad (5)$$

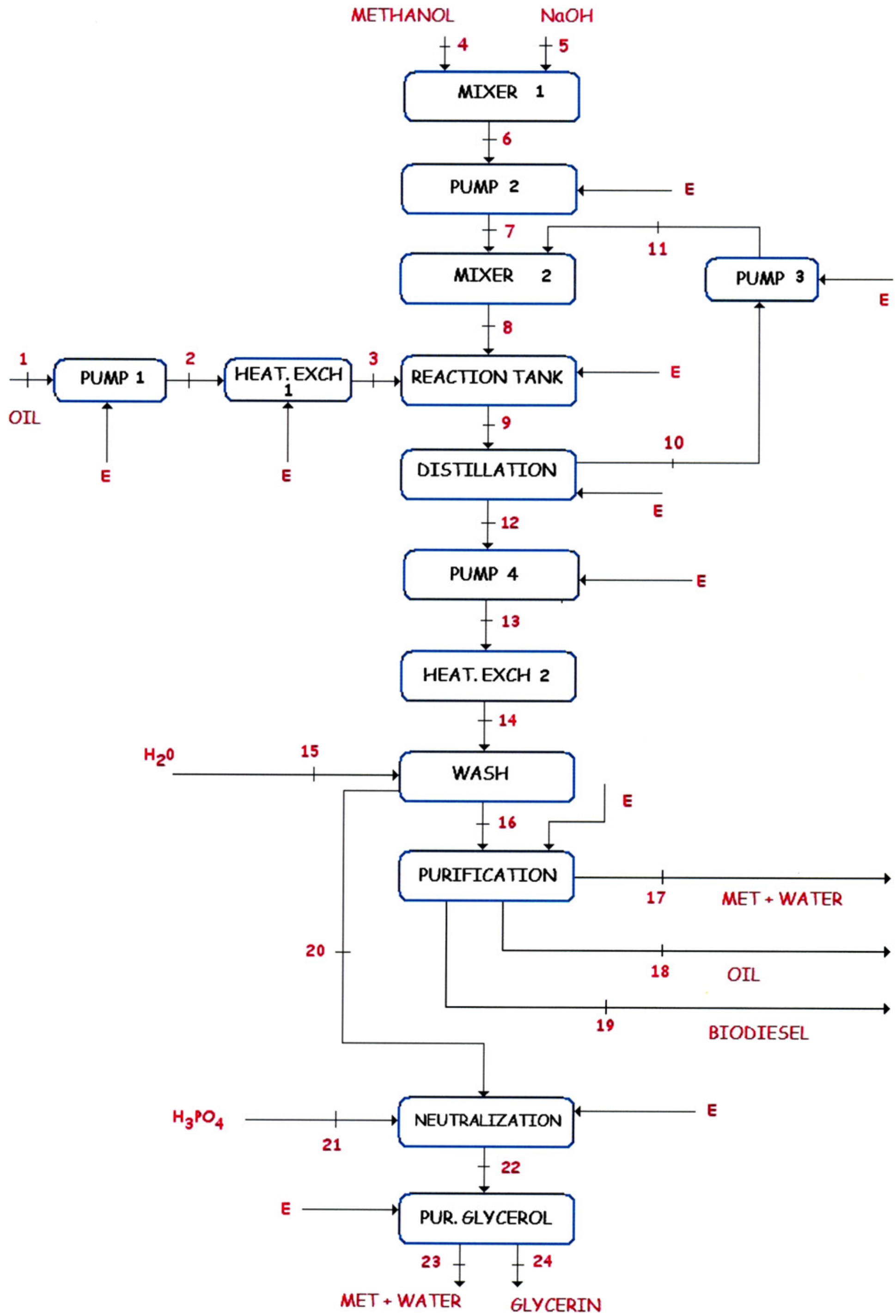


Fig. 2. Physical diagram of biodiesel production plant. (E=Electricity).

$$Y_{1.2} = Y_{0.2} = \frac{m_2 \times v \times \Delta P}{\eta_b} \quad (6)$$

$$Y_{1.1} = m_1 \times (ex_1 - ex_2) \quad (7)$$

UNIT 2: Hear exchanger 1 (EX1)

$$Y_{2.2} = Y_{0.1} = Heat \times duty \quad (8)$$

$$Y_{2.1} = Y_{1.1} \quad (9)$$

$$Y_{2.1} = m_2 \times (ex_2 - ex_3) \quad (10)$$

UNIT 3: Mixer 1 (M1)

$$Y_{3.1} = Y_{0.4} = m_4 \times ex_4 \quad (11)$$

$$Y_{3.2} = Y_{0.5} = m_5 \times ex_5 \quad (12)$$

$$Y_{3.1} = m_4 \times (ex_6 - ex_4) + m_5 \times (ex_6 - ex_5) \quad (13)$$

UNIT 4: Pump 2 (B2)

$$Y_{4.1} = Y_{3.1} \quad (14)$$

$$Y_{4.2} = Y_{0.6} = \frac{m_7 \times v \times \Delta P}{\eta_b} \quad (15)$$

$$Y_{4.1} = m_6 \times (ex_6 - ex_7) \quad (16)$$

UNIT 5: Mixer 2 (M2)

$$Y_{5.1} = Y_{4.1} \quad (17)$$

$$Y_{5.2} = Y_{6.1} \quad (18)$$

$$Y_{5.1} = m_7 \times (ex_8 - ex_7) + m_{11} \times (ex_{11} - ex_8) \quad (19)$$

UNIT 6: Pump 3 (B3)

$$Y_{0.7} = Y_{6,2} = \frac{m_{11} \times v \times \Delta P}{\eta_b} \quad (20)$$

$$Y_{6,1} = Y_{8.1} \quad (21)$$

$$Y_{6.1} = m_{11} \times (ex_{11} - ex_{10}) \quad (22)$$

UNIT 7: Reaction tank (TR)

$$Y_{7.1} = Y_{2.1} \quad (23)$$

$$Y_{7.2} = Y_{5.1} \quad (24)$$

$$Y_{0.8} = Y_{7,3} = \frac{m_9 \times C_p \times \Delta T}{\eta_{TR}} \quad (25)$$

$$Y_{7.1} = m_3 \times (ex_3 - ex_9) + m_8 \times (ex_8 - ex_9) \quad (26)$$

UNIT 8: Distillation (D)

$$Y_{8.1} = Y_{7.1} \quad (27)$$

$$Y_{8.2} = Y_{0.9} = \frac{m_9 \times C_p \times \Delta T}{\eta_D} \quad (28)$$

$$Y_{8.1} = m_{10} \times (ex_9 - ex_{10}) \quad (29)$$

Table 2
Chemical exergy of the main substance of the process. Molar ratio 6:1. Temperature 60 °C, pressure de 400 kPa.

Substance	Point	Flow (kg/h)	LHV (kJ/kg)	φ	Specific exergy—*ex* (kJ/kg)	Total exergy—*Ex* (kW)
Rapeseed oil	1	1050	39,700	1.07	42,575.42	12,417.83
Methanol	4	117.2	21,000	1.16	24,261.3	789.84
NaOH	5	10	–	–	1,873	5.20
Biodiesel	19	999.9	37,000	1.07	38,717.3	11,031.48
Glycerol	24	113.3	19,000	1.14	21,585.86	679.35
H_2O	15	11	–	–	50	0.15
H_3PO_4	21	15	–	–	1,061.22	4.42

Table 4
Irreversibilities of the system. Molar ratio 6:1. Temperature 60 °C, pressure 400 kPa.

UNIT	*I* (kW)	Unit	*I* (kW)
Pump 1	3,678	Distillation tank	1,438
Heat exchanger 1	31,511	Pump 4	6,768
Mixer 1	13,112	Heat exchanger 2	42,002
Pump 2	4,058	Wash tank	18,236
Mixer 2	50,415	Biodiesel purification	293,374
Pump 3	47,892	Neutralization tank	7,779
Transesterification tank	857,821	Gliceryn purification	59,044
Total	**1437,129**		

Table 5
Irreversibilities of the process for different molar ratios and reaction temperatures for production of biodiesel. Reaction pressure 400 kPa.

ITENS	Reaction time (°C)	*I* (kW)
Molar ratio 6:1	30	1463,112
	40	1454,451
	50	1445,790
	60	***1437,129***
Molar ratio 8:1	30	1573,758
	40	1564,596
	50	1555,434
	60	1546,271
Molar ratio 10:1	30	1587,361
	40	1577,681
	50	1568,001
	60	1558,321

Table 3
Thermodynamic characteristics of the biodiesel production plant. Molar ratio 6:1. Reaction temperature 60 °C, reaction pressure 400 kPa.

Point	*T* (°C)	*P* (kPa)	Flow (kg/h)	*h* (kJ/kg)	*s* (kJ/kg/°C)	Chem. *Ex* (kW)	*Ex* (kW)	*ex* (kJ/kg)
1	25	100	1050	−2612	0.137	12,417.832	12,417.832	42,575.424
2	25	400	1050	−2612	0.178	12,417.832	12,414.258	42,563.170
3	60	400	1050	−2543	0.533	12,417.832	12,403.477	42,526.207
4	25	100	117.2	−7473	1.454	789.840	789.840	24,261.300
5	25	100	10	−8766	−26.28	5.203	5.203	1873
6	25	100	126.7	−7574	−0.666	791.930	791.930	22,501.580
7	26.7	400	126.7	−7568	−0.260	791.930	787.886	22,386.650
8	26.7	400	238.4	−7523	0.677	1541.403	1533.815	23,161.643
9	60	400	1288.4	−3253	1.093	13,114.557	13,089.471	36,574.120
10	28.2	20	111.2	−6278	5.886	789.840	785.936	25,443.962
11	26.7	400	111.2	−7466	1.857	789.840	786.345	25,457.209
12	122.3	30	1177.2	−2721	1.397	12,378.541	12,360.265	37,798.976
13	122.3	200	1177.2	−2723	1.459	12,378.541	12,353.567	37,778.491
14	70	150	1177.2	−2839	0.980	12,378.541	12,362.305	37,805.216
15	25	100	11	−15810	0.364	0.153	0.153	50
16	60	110	1060	−2389	1.103	11,711.286	11,702.211	39,743.359
17	193.7	10	7.82	−4645	5.206	64.006	63.963	29,445.649
18	414.7	20	52.5	−1117	1.606	620.272	624.340	42,811.862
19	193.7	10	999.9	−2114	2.135	10,998.430	10,995.046	39,586.125
20	50	110	128	−8039	−1.636	647.215	642.010	18,056.551
21	25	100	15	−2326	−5.886	4.422	4.422	1061.224
22	60	110	122.3	−8270	0.207	651.942	649.675	19,123.700
23	56.2	40	9.02	−12660	1.438	22.146	22.126	8830.569
24	112	50	113.3	−8304	1.176	577.688	573.899	18,235.108

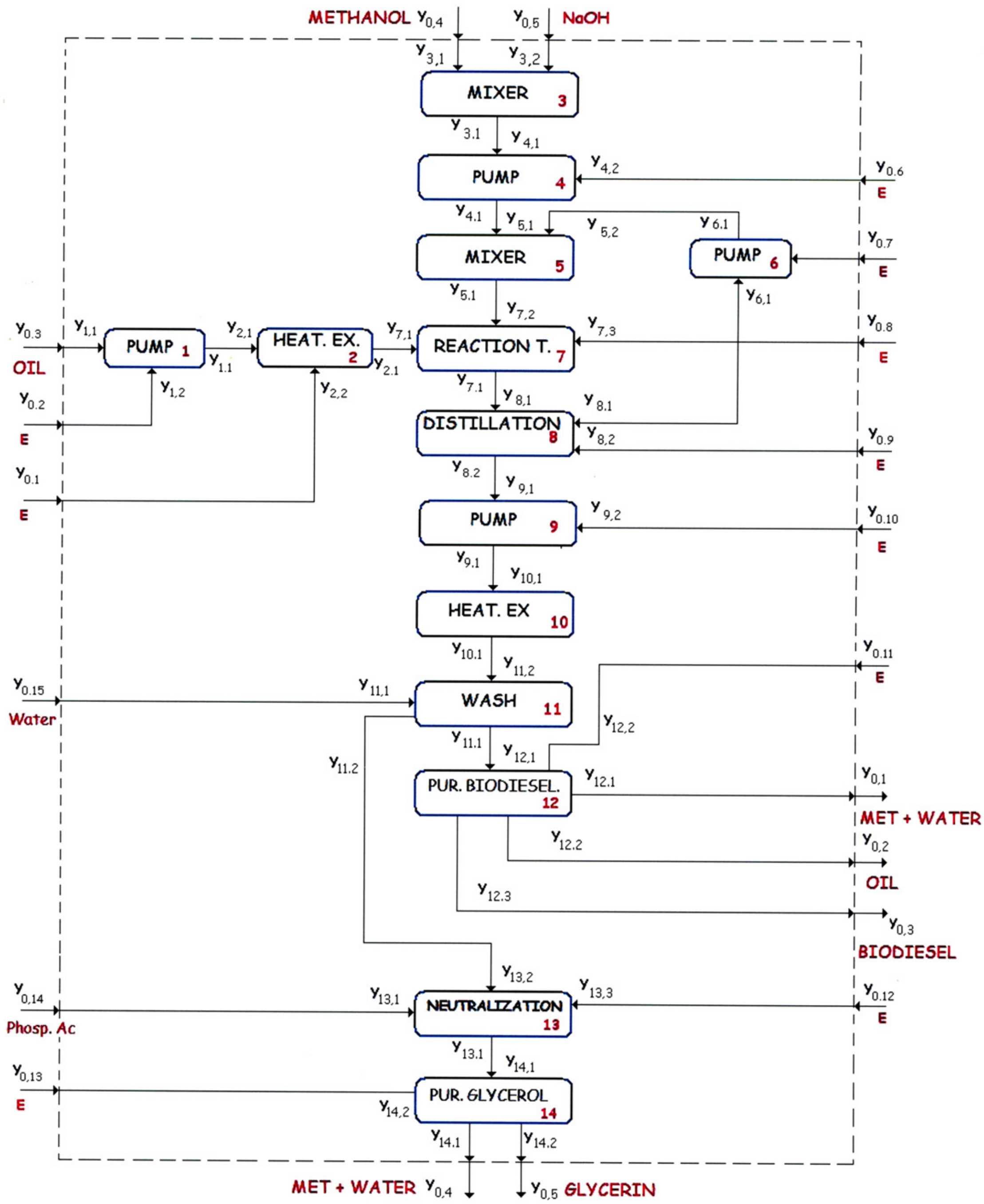


Fig. 3. Thermoeconomic functional diagram.

$$Y_{8.2}=m_{12}\times(ex_{12}-ex_9) \quad (30)$$

UNIT 9: Pump 4 (B4)

$$Y_{9.1}=Y_{8.2} \quad (31)$$

$$Y_{0.10}=Y_{9.2}=\frac{m_{13}\times\nu\times\Delta P}{\eta_b} \quad (32)$$

$$Y_{9.1}=m_{12}\times(ex_{12}-ex_{13}) \quad (33)$$

UNIT 10: Heat exchanger 2 (TC2)

$$Y_{10.1}=Y_{9.1} \quad (34)$$

$$Y_{10.1}=m_{14}\times(ex_{14}-ex_{13}) \quad (35)$$

$$Y_{10.2}=Y_{0.15} \quad (36)$$

UNIT 11: Wash (L)

$$Y_{11.1}=Y_{0.15}=m_{15}\times ex_{15} \quad 37)$$

$$Y_{11.2}=Y_{10.1} \quad (38)$$

$$Y_{11.1}=F_{16}\times m_{15}\times(ex_{16}-ex_{15})+F_{16}\times m_{14}\times(ex_{16}-ex_{14}) \quad (39)$$

$$Y_{11.2}=F_{20}\times m_{15}\times(ex_{20}-ex_{15})+F_{20}\times m_{14}\times(ex_{14}-ex_{20}) \quad (40)$$

$$F_{16}=\frac{m_{16}}{m_{15}+m_{14}} \quad (41)$$

Table 6
Values of exergy flows [kW], Molar ratio 6:1. Temperature 60 °C, pressure 400 kPa.

UNIDADE 1: Pump (B1)		**UNIDADE 9: Pump (B4)**	
$Y_{1.1}$	12,417,831	$Y_{9.1}$	400,528
$Y_{1.2}$	0,104	$Y_{9.2}$	0,069
$Y_{1.1}$	3,574	$Y_{9.1}$	6,699
UNIDADE 2: Heat exchanger (TC1)		**UNIDADE 10: Heat exchanger (TC2)**	
$Y_{2.2}$	20,731	$Y_{10.1}$	6,699
$Y_{2.1}$	3,574	$Y_{10.1}$	87,389
$Y_{2.1}$	10,781	$Y_{10.2}$	50,741
UNIDADE 3: Mixer (M1)		**UNIDADE 11: Wash (L)**	
$Y_{3.1}$	789,840	$Y_{11.1}$	0,153
$Y_{3.2}$	52,020	$Y_{11.2}$	8,739
$Y_{3.1}$	0,013	$Y_{11.1}$	673,592
UNIDADE 4: Pump (B2)	$Y_{11.2}$	689,747	
$Y_{4.1}$	0,013	**UNIDADE 12: Biodiesel Purification (PB)**	
$Y_{4.2}$	0,013	$Y_{12.1}$	673,591
$Y_{4.1}$	4,045	$Y_{12.1}$	63,962
UNIDADE 5: Mixer (M2)		$Y_{12.2}$	624,339
$Y_{5.1}$	4,045	$Y_{12.3}$	10,995,046
$Y_{5.2}$	0,409	$Y_{12.2}$	274,510
$Y_{5.1}$	98,183	**UNIDADE 13: Neutralization (N)**	
UNIDADE 6: Pump (B3)		$Y_{13.1}$	4,422
$Y_{0.7}$	0,016	$Y_{13.2}$	689,747
$Y_{6.1}$	343,798	$Y_{13.3}$	1,021
$Y_{6.1}$	0,409	$Y_{13.1}$	113,203
UNIDADE 7: Reaction Tank (TR)		**UNIDADE 14: Gliceryn Purification (PB)**	
$Y_{7.1}$	10,780	$Y_{14.1}$	113,203
$Y_{7.2}$	98,183	$Y_{14.1}$	22,125
$Y_{7.3}$	29,351	$Y_{14.2}$	573,899
$Y_{7.1}$	847,821	$Y_{14.2}$	5,394
UNIDADE 8: Distillation (D)			
$Y_{8.1}$	847,821	$Y_{8.1}$	343,798
$Y_{8.2}$	53,957	$Y_{8.2}$	400,528

$$F_{20} = \frac{m_{20}}{m_{15}+m_{14}} \quad (42)$$

UNIT 12: Biodiesel Purifier (PB)

$$Y_{12.2} = Y_{0.11} = \frac{m_{16} \times C_p \times \Delta T}{\eta_{PB}} \quad (43)$$

$$Y_{12.1} = Y_{11.1} \quad (44)$$

$$Y_{12.1} = Y_{0.1} = m_{17} ex_{17} \quad 45)$$

$$Y_{12.2} = Y_{0.2} = m_{18} ex_{18} \quad (46)$$

$$Y_{12.3} = Y_{0.3} = m_{19} ex_{19} \quad (47)$$

UNIT 13: Neutralization (N)

$$Y_{13.1} = Y_{0.14} = m_{21} \times ex_{21} \quad (48)$$

$$Y_{13.2} = Y_{11.2} \quad (49)$$

$$Y_{13.3} = Y_{0.12} = \frac{m_{22} \times C_p \times \Delta T}{\eta_N} \quad (50)$$

$$Y_{13.1} = m_{20} \times (ex_{22} - ex_{20}) + m_{21} \times (ex_{22} - ex_{21}) \quad (51)$$

UNIT 14: Glycerol Purifier (PG)

$$Y_{14.1} = Y_{13.1} \quad (52)$$

$$Y_{14.1} = Y_{0.4} = m_{23} ex_{23} \quad (53)$$

$$Y_{14.2} = Y_{0.5} = m_{24} ex_{24} \quad (54)$$

$$Y_{14.2} = Y_{0.13} = \frac{m_{22} \times C_p \times \Delta T}{\eta_{PG}} \quad (55)$$

4. Conclusion

In this Part I, the specific physical and chemical exergy of flows in each stage of the plant to produce biodiesel was calculated. The exergy calculation of increments and the calculation of irreversibilities in each stage of the plant as well as the overall system were included too. To calculate the increment of exergy and physical exergy of certain points, the simulation chemistry engineering software "HYSYS 3.2" was used. As for the chemical exergy, it was calculated based on the scientific thermodynamics literature. Through exergy calculation, it was found that the lowest irreversibility of the system refers to the process with a molar ratio of 6:1 and a reaction temperature of 60 °C in the process of transesterification. To continue with the thermoeconomic methodology proposed in this paper, the authors recommend the reader to read the second part of this work entitled "Development of a thermoeconomic methodology for the production of biodiesel. Part II: Exergetic manufacturing cost and biodiesel production cost incorporating carbon credits "submitted simultaneously with the Part I of this same journal.

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